SINOMENINE AND DISINOMENINE. XXI.
ON THE REACTION BETWEEN SINOMENINE AND FORMALDEHYDE.

By Kakuji GOTO, Hideo SHISHIDO and Reikichi INABA.

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When sinomenine (III) is boiled for two hours with ten times its weight of formaline (40%), two new bases can be isolated from the reaction mixture. As the base A is difficultly soluble in methyl alcohol and water and the base B is very soluble in these two solvents, they can be easily separated each other. The properties of these two bases are given in the following table.

Table 1.

	The base A (5-oxymethyl-sinomenine, I)	Dihydro-5-oxymethyl-sinomenine	The base B (1, 5-dioxymethyl-sinomenine, IV)
Mol. formula.	$C_{20}H_{25}NO_5$	$C_{20}H_{27}NO_5$	$C_{21}H_{27}NO_6$
Yield	30%	55%	10%
Solvent for recryst	Methyl alc.	Methyl alc.	Chloroform or methyl alc.
M.p.	269° (dec.)	244°	242° (fr. Me-A) 252° (fr. Chloroform)
$[\alpha]_D$	−40.71°	+73.03°	−74.39°
No. of methoxyls	2	2	2
Mol. weight	Monomolecular	—	Monomolecular
M.p. of oxime (all amorphous)	240–245°	215–225°	200–215°
M.p. of iodomethylate	223° (fr. Me-A)	205–220° (dec.)	210° (280 dec.)
$FeCl_3$ reaction	Green	Green	Brown
Diazo-reaction	2,000,000 th*	2,000,000 th	20,000 th
$FeK_3(CN)_6$ reaction	Faint	Faint	Almost no.
$HCOH$-H_2SO_4 reaction	Green→Brown	Blue violet	Green

* The figures show the dilution, at which the reaction is still visible.

The constitution of the base A, which is called to be 5-oxymethyl-sinomenine, is deduced from the following considerations.

1. The base A gives the diazo coupling reaction and ferric chloride reaction in the same strength as with sinomenine. The phehol group (4) and its para-position (1) must, therefore, be intact.

2. The base A is laevo-rotatory and its reduction product, dihydro-5-oxymethyl-sinomenine, is dextro-rotatory. This relation is the same with that of sinomenine (−) to dihydro-sinomenine (+) or to sinomenine hydrate (+). This shows that in the base A the original double linking of sinomenine must be kept intact.

3. By the acetolysis at 180°, the base A gives a nitrogen free product $C_{23}H_{22}O_5$ and methyl-ethyl amine. This shows that the reaction with formaldehyde did not occur on the methyl-amino-ethyl side chain.

In these state of affairs, there remain only four carbon atoms, which can be suspected to be able to enter the reaction with formaldehyde, namely, C(5), C(9), C(10) and C(14). Among these C(14) must be excluded, since the hydrogen atom on it must be lost in the course of acetolysis. The choice must be then made on C(5) C(9) and C(10). Of these three, C(5) is naturally the most susceptible point, where formaldehyde can react.

The reactivity of a methylene group, vicinal to a ketonic group, against aldehyde is well-known and is of two kinds. First, it is the linking together of the two methylene groups by means of the carbon atom of the aldehyde, that is the formation of the substance of the type of methylene bis-aceto-acetic ester. In the present case, this supposition is quite excluded, since the base A as well as its decomposition product are monomolecular.

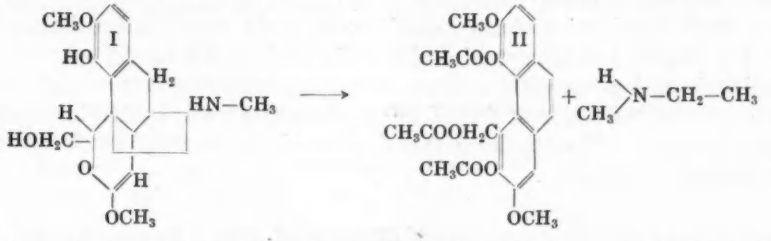
Secondly, it is the formation of the substance of the type of piperonylidene thebainone. Yet, this supposition does not reconcile with the results of the elemental analysis of the base A and of its decomposition product. Mereover, this type of reaction is known thitherto only with aromatic aldehydes, and not with the aliphatic.

The elemental analysis of the base A and of its decomposition product shows that the formaldehyde must have been introduced, in our case, as oxymethyl group. We have not many examples of this type of reaction in the literature, yet we can cite the case of methylol chinaldine[1] from chinaldine and formaldehyde in favor of our reasoning, although in the latter case, the reactivity of the methyl group is enhanced by the neighbouring $-C=N-$ group of the chinoline nucleus. The base A is called, accordingly, 5-oxymethyl-sinomenine.

By heating 5-oxymethyl-sinomenine with acetic anhydride in a sealed tube at 180° for fifteen hours, we obtained a nitrogen free substance $C_{23}H_{22}$

(1) Besthorn, *Ber.*, **39** (1906), 2329. Compare K. N. Welch, *J. Chem. Soc.*, **1930**, 257.

$O_8=C_{15}H_7(CH_3O)_2(CH_3COO)_3$ in 7% yield. The amine, splitted off, in this reaction, is also methyl-ethyl amine, as is the case with sinomenine[1].



By reducing 5-oxymethyl-sinomenine with $Pd+H_2$, we obtained dihydro-5-oxymethyl-sinomenine, whose properties are given in the third column of the Table 1. Yet, in an attempt to prepare this substance from dihydrosinomenine and formaline, the reaction products became syrupy.

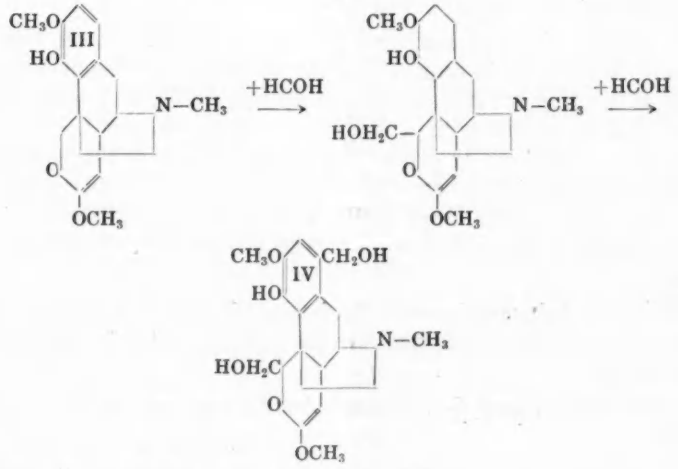
The constitution of the base B, 1, 5-dioxymethyl-sinomenine (III) can be deduced from the following three facts.

1. Its molecular formula is $C_{21}H_{27}NO_6$.

2. It gives diazo coupling reaction very faintly (1 : 20,000th or thereabout). A second oxymethyl group must, therefore, have been introduced in the para-position to the phenol group.

3. By boiling pure 5-oxymethyl-sinomenine with formaline for one hour, 1,5-dioxymethyl-sinomenine was produced in a tolerably good yield.

I.



(1) Goto, *J. of Agr. Chem. Soc. Japan*, **1** (1925), 50, 89.

Neither the acetolysis nor the reduction of 1,-5-dioxymethyl-sinomenine gave crystalline products.

Such introduction of oxymethyl group to the para- and ortho position of the phenol, had been studied already in 1894 by Manasse[1], who isolated saligenin and *p*-oxymethyl-phenol from the reaction mixture. He stated also that by the action of formaline on β-naphtol a dioxy-dinaphtyl-methan was produced. The studies in this line have been recently much advanced in relation to Bakelite.

Experimental Part.

1-Oxymethyl-sinomenine (1) and 1,5-Dioxymethyl-sinomenine (IV). When sinomenine (10 gr.) is boiled with formaline (50 c.c.; with the precipitate of oxymethylene), the base dissolves away slowly, changing the colour of the liquid into purple. After one hour, when the colour of the liquid turns brown, the boiling is discontinued and the mixture is diluted with water (100 c.c.). The reaction of the liquid is strongly alkaline. The bases are isolated from this mixture in the ordinary way. The raw yield is about 6 gr., i.e. 55% of the theoretical.

The raw product is recrystallised from boiling methyl alcohol (500 c.c.). 5-Oxymethyl-sinomenine crystallises out in stout prisms. Three recrystallisation is enough to obtain the substance in a pure state. M.p. 260° (dec.) The substance takes a purple colour at about 230°. Yield 3 gr. (ca. 30%). It does not react with Schiff's reagent.

The methyl alcoholic mother liquor is evaporated down, and the 5-oxymethyl-sinomenine is removed as far as possible. When long, hairy crystals of 1,5-dioxymethyl-sinomenine appear richly, it is evaporated to dryness and extracted with a little hot water. When the latter was shaken with chloroform or ether, the solvent as well as the aqueous layer is sometimes filled with the crystals of the substance. These crystals sinter at 95°, but melt at 252° (dec.) sharply. But, those crystals obtained by the evaporation of the solvents melt generally at 242°. Yield about 1 gr. (10%).

5-Oxymethyl-sinomenine was also isolated in a pure state from the cold mixture of sinomenine (1 gr.) and formaline (5 c.c.), after it was left stand for two weeks.

For the properties of 5-oxymethyl-sinomenine, see the first column of the Table 1.

(1) *Ber.*, **27** (1894), 2411.

Anal. Found: C=66.43, 66.55; H=6.87, 7.00; N=3.86, 3.88; methoxyls=16.62, 17.01, 16.58%. $C_{20}H_{25}NO_5$=359 requires: C=66.85; H=6.96; N=3.90; methoxyls=17.22%.

Mol. weight, measured cryoscopically in acetic acid: (0.5692÷15.9052)×(39×0.379) ×100=368; after Rast: (374÷4173)×(400÷9.53)×100=376.

Sp. rotatory power, in chloroform:

$[\alpha]_D^{29}=-(0.78\div0.479)\times(50\div2)=-40.71°$

Oxime: amorph. decomposing between 240–245° (Found: N = 7.52%. Calc. for $C_{20}H_{21}N_2O_4$: N=7.48%).

Iodomethylate: long needles from methyl alcohol. M.P. 223° (dec.); m.p. 190–195° (from water). (Found: I=23.91%. Calc.: I=25.35%)

For the properties of 1,5-dioxymethyl-sinomenine, see the third column of the Table 1.

Anal: C=64.85; H=6.70; N=3.55; methoxyls=15.57, 16.01%. $C_{21}H_{27}NO_6$ = 389 requires: C=64.78; H=6.99; N=3.59; methoxyls=15.93%.

Mol. weight, measured after Rast:

(358÷3612)×(400÷10.1)×100=392

Sp. rotatory power, measured in dilute methyl alcohol:

$[\alpha]_D^{30}=-(2.77\div0.4654)\times(25\div2)=-74.39$

Oxime: amorph. decomposing between 200–215°. Found: N=6.56%. Calc. for $C_{21}H_{28}N_2O_5$: N=6.93%.

Iodomethylate: crystallises out from methyl alcohol. M.p. 210°, but decomposes at 280–285°. Found: I=22.52%. Calc.: I=23.91%.

Decomposition of 5-Oxymethyl-sinomenine by Acetic Anhydride. 5-Oxymethyl-sinomenine is heated with 3–5 times its weight of acetic anhydride in a sealed tube for sixteen hours. The precipitate, formed by digesting the reaction mixture with much water, is dried and extracted with ether in a Soxleht's apparatus. The extracted substance is recrystallised first from methyl alcohol and then from glacial acetic acid. Long needles of pale yellow colour. M.p. 192–193°. Yield ca. 7%.

The above raw precipitate can be treated in the following away, also. It is dissolved in a small quantity of benzene and is added with petroleum ether in portions, until no precipitate is formed immediately after the addition. Then the mixture is filtered quickly and left stand. The needle crystals of the decomposition product appear after some time, and by its free evaporation some more is obtained.

This substance, presumably 5-acetoxy-methyl-diacetyl-sinomenol shows a green colour, when it is hydrolysed with alkali, but the hydrolysed solution does not give the sinomenol reaction[1]. This might be due to the intervention of oxymethyl group in C (5).

(1) This Bulletin, **4** (1929), 103.

Anal. Found: C=64.85; 64.66; H=5.09, 5.18; methoxyls=14.33%. $C_{23}H_{22}O_8$=426 requires: C=64.8, H=5.2; methoxyls=14.55%.

Mol. weight, measured after Rast:
(201÷3536)×(400÷5.48)×100=417.

Nitrogenous Substance. The aqueous part, from which the above precipitate was removed, was evaporated down and distilled with much caustic soda. The overdistilled amine was caught in dilute hydrochloric acid. The hydrochloride of amine, thus obtained, was once purified through absolute alcohol. Very hygroscopic. Yield about 0.3 gr. from 10 gr. of 5-oxymethyl-sinomenine. The chloroaurate of this amine crystallises well from water and melts at 179–180°. The chloroplatinate crystallises from alcohol and decomposes at 224°. We have, here, clearly, methyl-ethyl-amine.

Dihydro-5-oxymethyl-sinomenine. 5-Oxymethyl-sinomenine (2 gr.) was shaken in dilute hydrochloric acid solution with $PdCl_2$ (0.1 gr.) and charcoal (1 gr.) in a hydrogen atmosphere. The sorption of hydrogen amounted to 175 c.c. in two hours (a little more than 1 mol.). Dihydro-5-oxymethyl-sinomenine crystallises out in short prisms from methyl alcohol and melts at 244°. Yield 1.1 gr. (55% of the theoretical.).

Anal. Found: C=66.80; H=7.76; N=3.91%. $C_{20}H_{27}NO_5$=361 requires: C=66.48; H=7.48; N=3.88%.

Sp. rotatory power, measured in methyl alcohol+chloroform.

$[\alpha]_D^{29}$=+(1.92÷0.3286)×(25÷2)=+73.03

Oxime: amorph. decomposing at 215–225°. (Found: N = 7.34, 7.29%. Calc.: N=7.44%)

Iodomethylates: crystallisable from methyl alcohol. M.p. 205–220° (dec. from water). (Found: I=24.99%. Calc.: I=25.23%).

Transformation of 5-Oxymethyl-sinomenine into 1,5-Dioxymethyl-sinomenine. 5-Oxymethyl-sinomenine (1 gr.) was boiled with formaline (40%; 5 c.c.) for two hours. From the mixture of the bases, isolated in the way given above, we could isolate 1,5-dioxymethyl-sinomenine in ca. 10% yield. M.p. 242°. It gave only a brown colouration with ferric chloride in alcohol. Diazo-reaction was also strongly diminished (1 : 20,000th).

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART III.

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Introduction. Sodium sulphite oxidizes at a definite velocity, quite independent of its concentration, when air is passed into the solution at uniform velocity under certain conditions[1]. Following equations[2] were proposed to interprete the observed results from theoretical considerations.

$$k=\frac{v_0-v}{t-t_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$D=\frac{1}{4}k\times 10^{-4} \text{ moles/min.} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$D=\frac{60ap}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+S_0\right) \text{ moles/min.} \quad \ldots\ldots\ldots \quad (3)$$

$$k=\frac{24ap\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+S_0\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where k=the velocity constant calculated as a zero order reaction, v_0-v being the volume of sodium thiosulphate solution of 0.1000 normal equivalent to the amount of sodium sulphite oxidized during $t-t_0$ minutes,

D=the dissolution velocity of oxygen into water when the concentration of oxygen in the surface layer is kept to be zero,

a =the ratio of the total number of the molecules of oxygen which penetrate into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time, the concentration of oxygen in the surface layer being kept to be zero,

p =the partial pressure of oxygen,

M=the molecular weight of oxygen,

R =the gas constant,

(1) S. Miyamoto, this Bulletin, **2** (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40.

(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 123; S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229.

T =absolute temperature,
V =the volume of the gas passed per minute,
l =the depth of the center of a bubble when it just leaves the exit,
r =the radius of a bubble,
u =the ascending velocity of the bubble,
s_0=the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

If all the values in the equations 3 and 4 be kept constant except the value of the radius of the bubble, the equations can be simplified.

$$D=\frac{A}{ru}+B \quad \cdots\cdots (5)$$

$$k=\frac{A'}{ru}+B' \quad \cdots\cdots (6)$$

where A, B, A' and B' are constants.

The present research was carried out to ascertain if the equations 5 and 6 be acceptable.

Experimental. The apparatus and the method of the observation are quite the same as those described in the previous paper[1]. The bubbles of various magnitude were obtained by substituting the tube through which air is passed into the solution. The radius of the bubble and the corresponding ascending velocity given in the tables were obtained in quite the same manner as in the previous case[2].

The observed result is given in Table 1.

Table 1.

Temp.=25°C. Velocity of Air Passed=86.7 c.c./min.

Radius of a bubble r cm.	Time min.	v c.c.	$v_{calc.}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.23	3	16.16	—	0.249
	33	8.70	8.63	
	3	16.71	—	0.255
	43	6.52	6.67	
	3	44.63	—	0.253
	53	31.96	32.08	
	3	56.32	—	0.248
	53	43.90	43.77	
			Mean:	0.251

(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **5** (1930), 230.
(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 134.

Table 1.–(*Continued*)

Radius of a bubble r cm.	Time min.	v c.c.	$v_{calc.}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.29	3 43	18.92 9.86	— 9.92	0.227
	3 52	23.88 12.83	— 12.85	0.226
	3 53	37.60 26.28	— 26.35	0.226
	3 53	50.86 39.74	— 39.61	0.222
	3 53	65.54 54.39	— 54.29	0.223
				Mean: 0.225
0.36	3 43	17.25 9.10	— 9.01	0.204
	3 53	23.25 12.78	— 12.95	0.209
	3 58	37.61 26.36	— 26.28	0.205
	3 53	50.51 40.12	— 40.21	0.208
	3 53	60.97 50.89	— 50.67	0.202
				Mean: 0.206
0.41	3 43	18.04 10.61	— 10.24	0.186
	3 43	18.02 10.19	— 10.22	0.196
	3 54	23.33 13.13	— 13.38	0.200
	3 53	38.01 28.24	— 28.26	0.195
	3 55	62.13 51.75	— 51.99	0.200
				Mean: 0.195

Table 1.—(*Concluded*).

Radius of a bubble r cm.	Time min.	v c.c.	$v_{calc.}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.49	3	16.41	—	0.175
	43	9.42	9.33	
	3	23.02	—	0.175
	53	14.27	14.17	
	3	34.54	—	0.181
	53	25.49	25.72	
	3	46.55	—	0.181
	53	37.51	37.70	
	3	64.11	—	0.175
	53	55.34	55.26	
				Mean: 0.177

Table 2.

Temp.=25°C. Velocity of Air Passed=86.7 c.c./min.

r cm.	u cm./sec.	ru	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ $[=\frac{1}{2}k_{obs.}\times10^{-4}]$ moles./min.	$D_{calc.}$ moles./min.
0.23	23.7	5.451	0.251	0.252	6.28×10^{-6}	6.29×10^{-6}
0.29	23.1	6.699	0.225	0.226	5.63 ,,	5.64 ,,
0.36	23.1	8.316	0.206	0.204	5.15 ,,	5.10 ,,
0.41	23.1	9.471	0.195	0.193	4.88 ,,	4.82 ,,
0.49	23.1	11.319	0.177	0.180	4.43 ,,	4.50 ,,

The values of k and D calculated by the following equations are given in Table 2.

$$D_{\text{calc.}} = \frac{1.886 \times 10^{-5}}{ru} + 2.83 \times 10^{-6}$$

$$k_{\text{calc.}} = \frac{0.7543}{ru} + 0.1132$$

where the constants were obtained by the least square method. The observed values are plotted in Figs. 1 and 2.

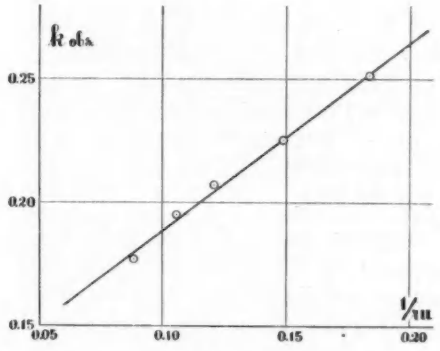

Fig. 1.

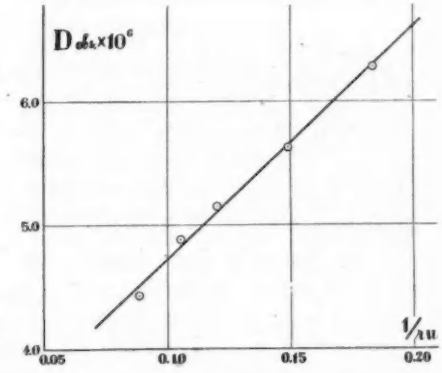

Fig. 2.

The result is thus quite favourable for the authors' considerations, as was expected.

Summary.

(1) The influence of the magnitude of the radius of the tube, through which air is passed, upon the oxidation velocity of sodium sulphite was observed.

(2) The theoretical considerations on the result was described.

The authors wish to express their appreciation for a grant from the Department of Education for the expenses of this research.

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UEBER DIE EINWIRKUNG DER KALILAUGE AUF DIE TETRACARBONSÄUREESTER VON DIMALONSÄURE-REIHE. (DARSTELLUNG VON AETHYL-PHENYLPROPIONSÄUREN).

Von Hsiung Tsai LO.

Eingegangen am 9. Oktober 1930. Ausgegeben am 28. November 1930.

Es wurde schon in früher Zeit von W.H. Perkin gezeigt,[1] dass sich *o*-Phenylendipropionsäure leicht durch Verseifung der *o*-Xylylendimalonsäureester mit konzentrierter alkoholischer Kalilauge erhalten lässt. In der ähnlichen Weise stellte Kipping *m*- und *p*-Phenylendipropionsäuren aus *m*- und *p*-Xylylendimalonsäureestern dar.[2] Mit einer bestimmten Absicht[3] habe ich mich damit beschäftigt, nach Perkin und Kipping Phenylendipropionsäuren in grösserer Menge herzustellen.

Im Verlaufe einer Anzahl von Versuchen wurde aber es gefunden, dass bei ortho-, sowie bei para-Verbindung die Phenylendipropionsäuren nur mit sehr geringer Ausbeute entstehen und die grösste Teile von sich dabei gebildeten Substanzen von anderen Eigenschaften sind. Aus diesen Tatsachen wurde es mir von Interesse, die Reaktionen noch eingehender und die neu entstandenen Substanzen näher zu untersuchen.

o- Xylylendimalonsäureester wurde mit einer 25% alkoholischer Kalilauge verseift und die Flüssigkeit mit verdünnter Schwefelsäure angesäuert. Durch Extraktion mit Aether, Abdestillation des Lösungsmittel und Erhitzung des zurückbleibenden Syrups auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung erhält man eine kristallinische Masse (A), ein Teil davon beim Behandeln mit Chloroform in Lösung geht, woraus sich eine Substanz vom Schmelzpunkt 103° scheidet. Auf Grund ihrer Zusammensetzung ($C_{11}H_{14}O_2$), Silbersalzbildung und Molekulargewichtsbestimmung ist sie mit grosser Wahrscheinlichkeit als *o*-Aethyl-phenylpropionsäure, $C_6H_4<^{C_2H_5(1)}_{CH_2CH_2COOH(2)}$, anzusehen, die um ein Mol. Kohlensäure ärmer als *o*-Phenylendipropionsäure ist. Genau wie bei *o*-Verbindung liess sich

(1) Bayer, Perkin, *Ber.*, **17** (1885), 452; Perkin, *J. Chem. Soc.*, **53** (1888), 18; Titley, *J. Chem. Soc.*, **1928**, 2578.

(2) Kipping, *J. Chem. Soc.*, **53** (1888), 21.

(3) In unserem Kubota-Laboratorium in "Institute of Physical and Chemical Research" sind seit einiger Zeit mehrere Versuche über die Bildungsfähigkeit der Ringe, welche am Benzolkern angebunden sind, im Gange. Einige Resultate darüber werden in kurzem veröffentlicht werden.

p-Aethyl-phenylpropionsäure, $C_6H_4<^{C_2H_5(1)}_{CH_2\cdot CH_2\cdot COOH(4)}$, aus *p*-Xylylendimalonsäureester gewinnen. Diese beiden Säuren sind meines Wissens noch nicht in der Literatur beschrieben und erscheinen zum erstenmale auf diesem einfachen Wege synthetisch dargestellt.

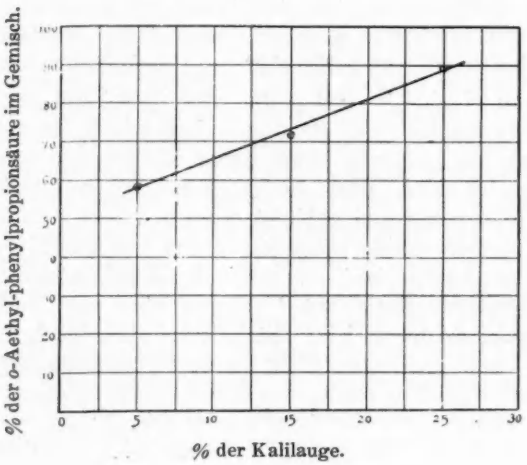
Beim Verseifen des *m*-Xylylendimalonsäureester unter den gleichen Bedingungen entstand dagegen keine Monocarbonsäure und das der Masse (A) entsprechende Produkt erwiess sich als fast reines *m*-Phenylendipropionsäure vom Schmp. 143–146°. Es ist nun vorzustellen, dass sich *m*-Verbindung verschieden von *o*- und *p*-Verbindungen verhalten müssen.

Nach Kipping[1] sind *m*- und *p*-Phenylendipropionsäuren destillierbar, ohne zersetzt zu werden. Ich habe auch beobachtet, dass *o*-Phenylendipropionsäure ebenso beständig gegen Hitze wie *m*- und *p*-Verbindungen ist. Daher ist es klar, dass Aethyl-phenylpropionsäuren nicht beim Erhitzen der Dikarbonsäuren gebildet werden. Dies wird auch dadurch gestützt, dass partielle Kohlensäure-Abspaltung von Dikarbonsäuren durch Erhitzen nicht mit Leichtigkeit, sondern in der Regel unter den Einwirkungen der Katalysatoren stattfindet.[2] Hierzu ist es auch beobachtet, dass *o*-Phenylendipropionsäure und ihr Diäthylester auch durch zwei stündiges Kochen mit konz. Kalilauge nicht Aethyl-phenylpropionsäure bilden. Aus diesen Tatsachen kann man mit Recht die Entstehung der Aethyl-phenylpropionsäuren durch die Annahme erklären, dass Xylylendimalonsäureester durch die Einwirkung von Kalilauge beim Verseifen gleichzeitig drei Mol. Kohlensäure abspalten. Eine solche Entziehung von Carboxylgruppe durch Kalilauge ist als von der gewöhnlichen Esterverseifung verschiedener Vorgang anzusehen. Eine ähnliche Erscheinung findet man bei 3-Phenyl-5-methyl-pyrrol-4-carbonsäureester, die sich durch Kochen mit alkoholischer Kalilauge in geringer Menge in 3-Phenyl-5-methyl-pyrrol überführen lässt.[3]

Es sei noch erwähnt, dass die Konzentration der Kalilauge scheint in der Bildung der Aethyl-phenylpropionsäuren eine wichtige Rolle zu spielen. Zur Untersuchung über den Zusammenhang zwischen der Bildungsleichtigkeit der Aethyl-phenylpropionsäuren und der Konzentration der Kalilauge wurde die Verseifung unter verschiedenen Bedingungen versucht. Die bei *o*-Xylylendimalonsäureester erzielten Ergebnisse sind aus folgenden Tabelle zu ersehen :

(1) Loc. cit.
(2) Seekamp, *Ann.*, **133** (1866), 253; Wisbar, *Ann.*, **262** (1891), 232; Mai, *Ber.*, **22** (1888), 2136; Farbenind, *A. G. Brit.*, **291** (1926), 326.
(3) Knorr, Lange, *Ber.*, **35** (1902), 3003.

% d. Kalilauge	% d. Monocarbonsäure im Gemische
5	58.52
15	72.16
25	89.70



Wie die obigen Zahlen zeigen, bildet die Monocarbonsäure leichter mit der Zunahme der Konzentration von Kalilauge. Daraus scheint es nun mir, dass Kalilauge von hocher Konzentration der Bildung von Phenylendipropionsäure ziemlich schädlich ist. Daher, wenn man die Phenylendipropionsäuren aus Xylylendimalonsäureestern mit besserer Ausbeute gewinnen will, hätte man besser getan, die Verseifung nicht mit konzentrierter, wie Perkin gezeigt hatte,[1] sondern mit verdünnterer Lauge auszuführen. Auch scheint es notwendig zu sein, die Verseifungsflüssigkeit nicht bis zum Trocknen zu verdampfen, sondern sogleich sie mit Wasser zu verdünnen, anzusäuern und dann mit Aether auszuschütteln. Durch Verdampfung der ätherischen Lösung und Erhitzung des Syrups auf 150–155° geht die Xylylendimalonsäure glätter in Phenylendipropionsäure über.

Verseift man Xylylendimalonsäureester mit konzentrierter alkoholischer Kali, verdünnt mit Wasser, säuert mit Schwefelsäure an und

(1) *J. Chem. Soc.*, **53** (1888), 18.

extrahiert mit Aether, so ist es vorzustellen, dass in dem Aether extrakt Xylylendimalonsäure, Phenylendipropionsäure und Aethyl-phenylpropionsäure gemischt vorhanden sind. Beim Verjagen des Lösungsmittel und Erhitzen des zurückbleibenden Syrups auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung würde nun alle Tetracarbonsäure in Phenylendipropionsäure übergehen, diese aber, wie oben beschrieben, wird nicht bei diesen Temperaturen zersetzt (Schmelzpunkt von Phenylendipropionsäure =168°). Daher muss die erstarrte Masse im wesentlichen aus Di- und Monocarbonsäuren bestehen. Die Menge von beiden Säuren in dem Gemische lässt sich also aus Silbersalz von Säuregemisch wie folgend abschätzen:

Setzt man

$M_1 = C_6H_4(C_2H_5)\,(CH_2CH_2COOAg) = 284.98$,

$M_2 = C_6H_4(CH_2CH_2COOAg)_2 = 435.76$,

$A_1 = Ag = 107.88$,

$A_2 = 2Ag = 215.76$,

s = Gewicht des Silbersalzgemisches,

a = Gewicht des zurückbleibeden Silbers,

x = Fraktion von Aethyl-phenylpropionsäure,

$1-x$ = Fraktion von Phenylendipropionsäure,

so erhält man

$$\frac{sx}{M_1}A_1 + \frac{s(1-x)}{M_2}A_2 = a,$$

$$x = \frac{A_1M_1}{A_2M_1 - A_1M_2} - \frac{aM_1M_2}{s(A_2M_1 - A_1M_2)}$$

$$= 4.2515 - 8.5886 \cdot \frac{a}{s}.$$

Beschreibung der Versuche.

I. o-Aethyl-phenylpropionsäure, o-Xylylendimalonsäureester wurde mit einem Ueberschuss von 25% alkoholischer Kalilauge drei Stunden lang auf dem Sandbade gekocht. Die Flüssigkeit wurde mit Wasser verdünnt und dann mit Aether ausgeschüttelt, um den unverseiften Ester zu entfernen. Die alkalinische Lösung wurde mit verdünnter Schwefelsäure angesäuert und mit Aether ausgezogen. Durch

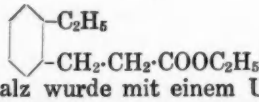
Trocknen des Auszugs über Calciumchlorid und Verdunsten des Lösungsmittel erhält man einen gelblichen Syrup, der beim Erhitzen auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung in eine kristallinische Masse erstarrte. Beim Behandeln mit Chloroform geht *o*-Aethyl-phenylpropionsäure in Lösung. Die beim Verjagen des Lösungsmittel zurückbleibende Säure schmilzt nach Umkristallisieren aus Wasser bei 103°. Farblose Nadel. Schwer löslich in kaltem Wasser, leicht löslich in Aether, Chloroform, Alkohol, und Benzol. Sublimiert über Schmelzpunkt.

Anal. 3.996 mg. Subst. gaben 10.816 mg. CO_2 und 2.912mg, H_2O. (Gefunden: C=73.82; H=8.09. Berechnet: C=74.11; H=7.92%).

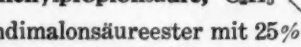
Molekulargewichtsbestimmung (nach Karl Rast). Subst. 0.309 mg., Kampher 7.677 mg., Depression 9.3°. (Gefunden: M=173.1. Berechnet: M=178.1).

Silbersalz der Aethyl-phenylpropionsäure. Versetzt man eine neutrale Lösung des *o*-äthyl-phenylpropionsauren Ammoniums mit einem Ueberschuss von 5% Silbernitrat-Lösung, so fällt das Silbersalz als weisser Niederschlag aus. Zur Analyse wurde das Salz über Schwefelsäure getrocknet. Amorpher Pulver.

Anal. 0.1387 gr. Subst. gaben 0.0527 gr. Ag. (Gefunden: Ag=38.00. Berechnet für $C_{11}H_{13}O_2Ag$: Ag=37.86%).

o-Aethyl-phenylpropionsäureester,  Das über Schwefelsäure gut getrocknete Silbersalz wurde mit einem Ueberschusse von Aethyljodid und Aether auf dem Wasserbade 4 Stunden lang erwärmt. Dann nach Zusatz von weiterem Aether filtriert und das Silberjodid mit Aether ausgewaschen. Zur Isolierung des Esters wurde die ätherische Lösung nach Trocknen über Calciumchlorid möglichst eingeengt und der Destillation im Vakuum unterworfen. Farblose Flüssigkeit, Siedepunkt 131°/10 mm.

Anal. 4.306 mg. Subst. gaben 11.835 mg. CO_2 und 3.548 mg. H_2O. (Gefunden: C=74.96; H=9.15. Berechnet: C=75.73; H=8.73%).

II. *p*-Aethyl-phenylpropionsäure,  Verseift man *p*-Xylylendimalonsäureester mit 25% alkoholischer Kalilauge und behandelt die Reaktionsprodukte in genau gleicher Weise wie bei *o*-Verbindung, so erhält man *p*-Aethyl-phenylpropionsäure. Sie lässt sich aus Wasser als farblose Nadeln umkristallisieren. Schmelzpunkt 114–115°. Leicht löslich in Aether, Chloroform, Alkohol und Benzol, schwer löslich in kaltem Wasser.

Anal. 3.791 mg. Subst. gaben 10.227 mg. CO_2 und 2·835 mg. H_2O. (Gefunden: C=73.58; H=8.31. Berechnet: C=74.11; H=7.92%).

Molekulargewichtsbestimmung (nach Karl Rast). Subst. 0.368 mg., Kampher 2.720 mg., Depression 29.3°. (Gefunden: M=184.7. Berechnet: M=178.1).

Silbersalz der p-Aethyl-phenylpropionsäure. Das Silbersalz lässt sich aus der neutralen Ammoniumsalzlösung mit Silbernitrat ausfällen. Amorpher, weisser Pulver. Beim Erhitzen über 100° wird es braun gefärbt. Zur Analyse wurde das Salz über Schwefelsäure getrocknet.

Anal. 0.232 gr. Subst. gaben 0.0872 gr. Ag. (Gefunden: Ag=37.49. Berechnet für $C_{11}H_{13}O_2Ag$: Ag=37.76%).

p-Aethyl-phenylpropionsäureester, $C_2H_5-C_6H_4-CH_2 \cdot CH_2 \cdot COOC_2H_5$. Dieser Ester lässt sich aus Silbersalz der *p*-Aethyl-phenylpropionsäure und Aethyljodid wie bei ortho-Verbindung erhalten. Farblose Flüssigkeit, Siedepunkt 141°/15 mm.

Anal. 3.837 mg. Subst. gaben 10.521 mg. CO_2 und 3.205 mg. H_2O. (Gefunden: C=74.78; H=9.28. Berechnet: C=75.73; H=8.73%).

III. Die Einwirkung der Kalilauge auf die Bildung von o-Aethyl-phenylpropionsäure. *o*-Xylylendimalonsäureester wurde mit (1) 5%, (2) 15%, (3) 25% alkoholischer Kalilauge verseift. Nach zwei stündigem Kochen, Verdünnen mit Wasser und Ausschütteln mit Aether wurde die Flüssigkeit mit verdünnter Schwefelsäure angesäuert und dann mit Aether extrahiert. Das Extrakt wurde über Calciumchlorid getrocknet. Die durch Abdestillation des Lösungsmittel und Erhitzen des zurückbleibenden Syrups erhaltene kristallinische Masse wurde in möglichst wenig verdünnter Natronlauge gelöst, filtriert und mit Schwefelsäure ausgefällt. Nach Umkristallisieren aus kleiner Menge Wasser wurden die Säuregemische in ihre Ammoniumsalze und dann mit Silbernitrat in die Silbersalzgemische übergeführt. Zur Analyse wurden die Salze über Schwefelsäure getrocknet.

(1) 5% KOH: 0.0752 gr. Silbersalzgemisch (*s*) gaben 0.0321 gr. Silber (*a*).
Fraktion von Aethyl-phenylpropionsäure im Gemische

$$=x=4.2515-\frac{0.0321}{0.0752}\times 8.5886=0.5852, \text{ oder Monocarbonsäure}=58.52\%.$$

(2) 15% KOH: 0.0900 gr. Silbersalzgemisch gaben 0.0350 gr. Silber.
Monocarbonsäure=72.16%.

(3) 25% KOH: 0.0776 gr. Silbersalzgemisch gaben 0.0304 gr. Silber.
Monocarbonsäure=89.70%.

Aus diesen Zahlen geht es hervor, dass sich die Menge an Monocarbonsäure mit der Zunahme der Konzentration von Kalilauge vermehrt. Die Resultate sind schon oben graphisch wiedergegeben.

IV. Die Einwirkung der Kalilauge auf *o*-Phenylendipropionsäure und ihren Ester. Die zu unten beschriebenen Versuchen verwandete *o*-Phenylendipropionsäure enthält von vornherein etwas *o*-Aethyl-phenylpropionsäure. Nämlich:

0.2407 gr. aus dieser Probe hergestelltes Silbersalzes gaben 0.1166 gr. Silber. (Gefunden: Ag=48.44. Berechnet für $C_6H_4(CH_2CH_2COOAg)_2$: Ag=49.51%).

(1). Die Dipropionsäure wurde mit einer 20% alkoholischen Kalilauge zwei Stunden lang gekocht. Beim Ansäuern, Ausschütteln mit Aether und Verdunsten des Lösungsmittel wurde Säuresubstanz wieder erhalten. Sie wurde in bekannter Weise in das Silbersalz übergeführt.

0.2594 gr. Silbersalz gaben 0.1260 gr. Ag. (Gefunden: Ag=48.53%).

Aus diesem Resultat sieht man, dass die Phenylendipropionsäure nicht durch die Einwirkung von Kalilauge zersetzt wird.

(2). Das Silbersalz wurde mit Aethyljodid und Aether in den Aethylester umgewandelt. Der Ester wurde dann mit einer 20% igen alkoholischen Kalilauge während zwei Stunden gekocht. Behandelt man die Reaktionsprodukten in oben beschriebener Weise erhält man schliesslich wieder eine sauere Substanz, die sich nach Umkristallisieren aus Wasser als *o*-Phenylendipropionsäure ergab und dann in ihres Silbersalz übergeführt wurde.

0.2347 gr. Silbersalz gaben 0.1145 gr. Ag. (Gefunden: Ag=48.79%).

Daraus wird es klar, dass auch der *o*-Phenylendipropionsäureester nicht durch Kali Kohlensäure abspaltet.

Zusammenfassung.

1. Es wurde beobachtet, dass *o*- und *p*-Xylylendimalonsäureester beim Verseifen mit konzentrierter alkoholischer Kalilauge leicht unter Abspaltung von drei Mol. Kohlensäure die Kaliumsalze von *o*- und *p*-Aethylphenylpropionsäuren bilden. Man muss deshalb Sorgfalt auf der Konzentration der Lauge verwenden, wenn man durch Verseifung dieser Dimalonsäureester *o*- und *p*-Phenylendipropionsäuren gewinnen.

2. Diese Versuche zeigen eine Darstellungsmethode von *o*- und *p*-Aethyl-phenylpropionsäuren, welche noch nicht nach anderen Verfahren dargestellt sind.

3. Aethyl-phenylpropionsäuren scheinen mit der Zunahme der Konzentration von Kalilauge leichter zu entstehen.

4. Im Gegensatz zu den *o*– und *p*–Verbindungen erhielt man keine Monocarbonsäure aus *m*–Xylylendimalonsäureester in diesen Versuchen.

Es sei mir gestattet, meinem hochverehrten Lehrer Herrn Prof. Dr. B. Kubota für seine wohlwollende Freundlichkeit, mit der er so eifrig mich leitete, meinen wärmsten Dank auszusprechen.

Aus der "Institute of Physical and
Chemical Research," Tokyo.

ON THE TRUE NATURE OF "PER-ACIDS" AND THE ALLEGED "ACID NUCLEUS THEORY."[1]

By Shin'ichirô HAKOMORI.

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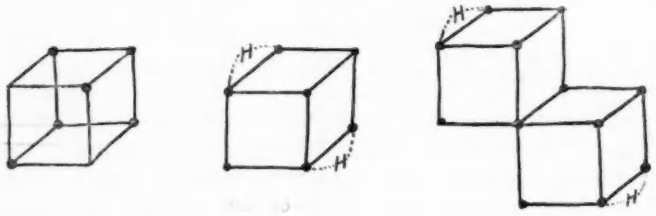
Several years ago, the present author commenced the researches to make clear the true nature of the "Per-acid." The results obtained in the researches have already been reported time to time in three former papers.[2] In the present communication, the author proposes a new hypothesis concerning the structure of the "Per-acid," which explains the experimental results obtained by the author as well as those obtained by others.

"Per-acids" are "Acids" which are formed when "Oxy-acids" are treated with hydrogen peroxide or which turn into "Hydrogen peroxide" under suitable treatment. The "Permanganic" and "Perchloric" -acids, therefore, do not belong to this group although these are also prefixed with "Per-." When the "Oxy-acids" are "metallic," very sensitive and characteristic colorations are frequently produced. This is the reason why "Per-acids reactions are recommended for the detection of such metals in qualitative analysis. As for the other characteristics of "Per-acids," the unstability of these compounds may be mentioned. The literatures on this subject are so many and so divergent with each other that it is very difficult here to enumerate them briefly. The readers, however, may refer to the excellent book of T. Slater Price[3] on this subject.

(1) Published in Japanese in the *Journal of the Chemical Society of Japan*, **50** (1929), 231.
(2) Ibid., **48** (1927), 441; **49** (1928), 511; **50** (1929), 221.
(3) "Per-acids and their salts", Longmans, Green & Co., London (1912).

The structure of the compounds should be considered very complicated but it can not be denied that it is related very closely in the fundamental aspects to that of the "Oxy-acids." Reflection upon the true nature of Oxy-acids," therefore, is required in order to make clear the true nature of "Per-acids." The present author here proposes a new hypothesis called "Acid nucleus theory" for these purposes. The theory starts from the following three postulates.

Postulate I. The natures of the elements which belong to the first, second and third short periods and the "Oxy-acid forming elements" are mainly determined by the arrangement of electrons of the outer shell as G. N. Lewis[1] suggested in his "Octet theory." Accordingly, for example, oxygen, water and hydrogen peroxide possess the following electronic configurations on the outer shells, the black dot showing an electron.



Postulate II. The valences are divided into the following three classes:

(1) Covalence, (2) Electrovalence, (3) Induction-valence.

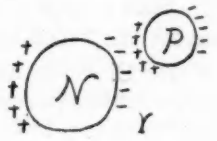
Among these (1) and (2) have already been fully considered by G. N. Lewis[2] and are produced by the co-owning and locomotion of electrons respectively. Both of these are measurable with integral numbers. The combinations produced by (1) are stronger and firmer than those produced by (2), because, in the former cases, electrons are co-owned. The valence (3), is produced by the phenomenon of electric induction,[3] and is not measurable by integral numbers.

(1) G. N. Lewis, *J. Am. Chem. Soc.*, **38** (1916), 762.

(2) Loc. cit.

(3) Such conceptions as these may exist in everyman's thought implicitly. Cf. G.N. Lewis, *J. Am. Chem. Soc.*, **35** (1913), 1448. The author has attempted only to give a somewhat systematic external form to these conceptions with reference to the problem attempting the clearing up of the true nature of "Per-acid."

Assuming that N is a particle electrically neutral, P is a particle in a polarized state, and the latter approaches to the former, N is naturally polarized due to the electronic induction between the two, where P is called the "Inductor" and N, the "Acceptor."



The force F between them is given by

$$F = \frac{D_P \times D_N}{Kr^2}$$

where D_P denotes the electrical displacement in P, D_N the same in N, r the distance between the two, and K the dielectric constant of the medium.

The author's "Induction valence" is nothing but such a force as represented by F. Now, consider a case in which a molecule formed by such a combination is moved to the gaseous space from an aqueous solution. Then the dielectric constant of the medium will continuously change, so also the force F. The valence, therefore, can not be equal in the aqueous solution and in the gaseous state.

Next, any arbitrary inductor is not always capable of inducing any arbitrary acceptor. As to this relation, the following postulate is given. Every inductor radiates its own characteristic electromagnetic wave say an inducing wave. And the wave-length of the characteristic wave is determined by the electronic configuration and the mass of the inductor. When the acceptor receives the wave, there are two cases in which an electrical displacement is either produced or not. The former case is nothing but a phenomenon called "Electrical induction."

When the electronic configuration of an acceptor is of unsymmetrical arrangement, electrical displacement will readily be accomplished and therefore, it is easily induced.

And when the mass of the acceptor is large or the domain occupied in the medium is accordingly large, the specific effects exerted over the mass will be comparatively small as though the same amount of electrical displacement is produced as in the case in which the mass is small. In this case, therefore, the acceptor is not easily induced.

Potulate III. The atom of the "Acid forming element" has so many electrons at the corners of a surface octet as is equal to the valency of the element as an acid. The element has a remarkable tendency to combine with oxygen by a co-valence, namely, by co-owning the electrons to fill the vacancy in the octets and thus makes the whole mass stable.

Such a mass of octets is called "Acid nucleus." For example, the "Acid nucleus" of hexavalent sulphur is given by: Where ⊗ shows an octet of oxygen combined with sulphur by co-owning two pairs of electrons. The "Acid nucleus" is not, however, to be hastily recognized at once as the same as the "Acid anhydride." The former is chiefly to be considered as a structural unit and the latter as a name of material.

Then, starting from the three postulates mentioned above, the "Acid nucleus theory" will be explained with reference to the data of a few "Oxy-acids" already existing.

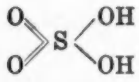
For the sake of convenience a part of the periodic table will be given below.

III	IV	V	VI
B	**C**	**N**	O
Al	Si	**P**	**S**
Sc	**Ti**	**V**	**Cr**
Ga	Ge	As	**Se**
Y	**Zr**	**Nb**	**Mo**
In	**Sn**	Sb	Te
La (?)	Ce	—	—
—	—	—	—
Yb	—	**Ta**	**W**
Tl	Pb	Bi	—
—	Th	—	**U**

In this table, those printed in Gothic type indicate the elements capable of forming "Per-acids." Glancing over the table, one will notice that all the elements capable of forming both "Oxy-acids" and "Per-acids" belong to the fourth, fifth and sixth groups in the table with a few exceptions.

For example, sulphur and phosphorus which form (A) sulphuric acid and (B) phosphoric acid, the most popular "Oxy-acid," belong to the sixth and fifth groups, respectively. They are explained here with the theory.

(A) *Sulphuric Acid.* The constitution of sulphuric acid is commonly represented as follows:



..... (1)

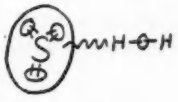
According to this formula, however, the two oxygen atoms out of four and the two hydrogen atoms must be of the same behavior. But in reality, the three oxygen atoms out of four are of the same behavior, e.g.

$$H_2SO_4 + PCl_5 = SO_3 + POCl_3 + 2HCl,^{(1)}$$

and one of the two hydrogen atoms dissociates more readily into an ion than the other.

The formula (1), therefore, is not pertinent to the real state of sulphuric acid molecule, regarding to even the above two points.

Now, according to "Acid nucleus theory," the "Acid nucleus" of sulphuric acid must be such that has been shown previously and be electrically neutral. In this case, a molecule of water, acting as an inductor, approaches to the "Acid nucleus," polarized the latter and combine with an "Induction valence." The above mechanism of the combination is shown schematically in the following figure, in which the wave line indicated the induction valence.



From the above view, the correct answers to the two facts above mentioned will be readily made: The three oxygen atoms out of four are of the same behavior because the combination within the "Acid nucleus" is accomplished by covalence and is, therefore, stronger and firmer than in the other part; and one of the two hydrogen atoms dissociates more readily into an ion than the other because the part ∿∿HOH is itself polarized and the two hydrogen atoms are not to be of the same behavior, and as is clear from postulate II the valency exerted between the "Acid nucleus" and water is not always to be measurable by a definite integral number. The large dehydrating power and the large heat of dilution of sulphuric acid mean a large Coulomb's force exerted between the "Acid nucleus" and water molecule, that is the valency force is large.

(B) *Phosphoric Acid.* The peculier property of phosphoric acid is that there are several kinds which are derived from the same pentavalent phosphorus; for example, there are: (a) orthophosphoric acid, (b) pyrophosphoric acid and (c) metaphosphoric acid.

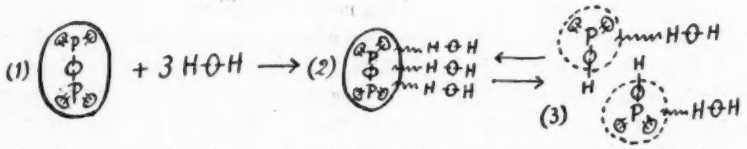
(1) Gerhardt and Chiozza, *Compt. rend.*, **36** (1853), 1050. In this case, SO_3 combines further with HCl and turns into SO_3HCl. Cf. Ostwald, "Grundlinien der anorg. Chemie", Leipzig (1922), 344.

(b) is formed through dehydration of (a) by heating up to 213°C.; (c) is formed when (a) and (b) are thoroughly dehydrated by heating until no more water escapes or when phosphorus pentoxide is dissolved in cold water. These three substances are changeable with one another and the change is mainly controlled by the content of water. It is, therefore, most probable that, when the solution of any of them is boiled for a long time, it contains all three substances as the solutes. The constitutional formula for (a) is commonly represented as below:

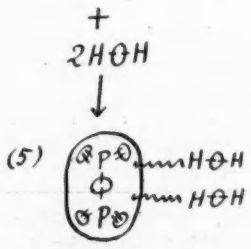
$$O=P\begin{matrix}OH\\OH\\OH\end{matrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The formula (2) is not also pertinent to the real state of phosphoric acid just as the formula (1) is not so to that of sulphuric acid. From the "Acid nuleus theory," the "Nucleus" of phosphoric acid is given as below:

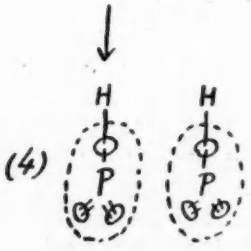
In this case, two atoms of pentavalent phosphorus gather together in order to render the "Nucleus" stable. But this "Nucleus" is not always the most stable, because it consists of octets of an odd number. It has, therefore, a tendency to separate itself further into two parts in order to form octets of an even number if possible and to combine with water by "Induction valence," as shown below:



"Phosphoric acid nucleus" Water Orthophosphoric acid Orthophosphoric acid



Pyrophosphoric acid

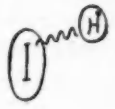


Metaphosphoric acid

As stated above, the "Acid nucleus theory" explains most conveniently the various properties of the "Oxy-acids." It must, therefore, be considered that, to explain the true nature of oxy-acid the present theory is more suitable than the commonly given formula.

The theory of indicator will also be explained easily by the theory as follows. A definite colour change is produced when the concentration of hydrogen ions has a definite value. All indicators are, in the widest sense, acid. The "Acid nucleus" (I) of such an acid can, therefore, be considered.

The above explanation is nothing but an electrical phenomenon produced by a hydrogen ion, an "Inductor" upon the "Acid nucleus" (I), an acceptor. From the standpoint of "Induction valence," the definite hydrogen ion concentration means a definite "inducing" force which produces a definite amount of electrical displacement in (I), or in other word the definite tautomeric change and colour change.



As mentioned above, it has become clear that the "Acid nucleus theory" is most conveniently applied not only to the problem of "Oxy-acids" but also to the theory of indicator. From this same standpoint, a consideration will be given to the true nature of "Per-acids."

As is readily known from Postulate 1, both water and hydrogen peroxide are typical polar compounds. For example, the dielectric constant of the former is 80, the latter is 92.8. Both of these are, therefore, capable of playing the rôle as inductors. This is the reason why there is formed, on the one hand, water of crystallization and hydrogen peroxide of crystallization on the other. In other words, both of these are no other than compounds of the same type being reviewed from a standpoint of "Induction valence." As already stated, if the substance which is formed by combination of "Acid nucleus" with water by "Induction valence" is "Oxy-acid," then "Per-acid" is nothing but a substance which is formed by combination of "Acid nucleus" with "Hydrogen peroxide" by the same valence. The meaning of the above statement will be explained more fully in the following.

Now, by the readiness of formation of "Per-acids" it is perceived that, in the periodic table already given, the elements whose atomic weights are small show a remarkable tendency to form "Oxy-acids" rather than "Per-acids." The latter are formed only under special suitable conditions, as in the case of "Persulphuric acid." But when the atomic weights become larger such as in the case of Ti and V, "Per-acids" are formed most readily by the simple addition of hydrogen peroxide to the acid solutions of the „Oxy-acids" and the readiness with which "Per-acids" are formed

reaches a maximum in the case of Cr. In all these cases "Per-acids" possess deep characteristic colourations. This is the reason why the "Per-acids reaction" is most frequently recommended in qualitative analysis for the detection of these elements. And finally, as the atomic weights increase further, the readiness of formation and the depth of the colourations decrease, but the stability of "Per-acids" increases. In the case of uranium we find the most stable metallic "Per-acids." In other words, in the case of those elements which readily form "Per-acids" by simple addition of hydrogen peroxide to the solution, the colourations produced are deep but the stability is small. On the contrary, in the case of those elements which form "Per-acids" only under limited conditions, the colourations produced are light but the stability is large. This is the fundamental rule which governs the formation of "Per-acids." The experimental results cited below clearly indicate that the above rule is valid.

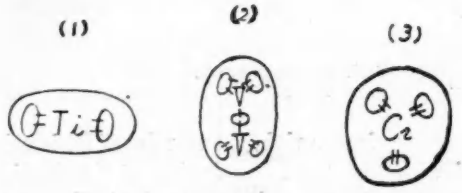
No. of exp.	Atomic weight of the acid forming element	Initial conc. of H_2O_2 (mol.)	The ratio of metallic acid present and hydrogen peroxide 1:1	The rise in potential (V.)	The conc. of H_2O_2 in the presence of metallic acids as calculated from the rise in potential (mol.)	The approxim. partial vapor press. of H_2O_2 in the presence of metallic acids estimated from the photographic action (atm.)	The colours of "Per-acids"
1	U = 238	0.117	$UO_3 : H_2O_2$	0.0047	0.117×0.69	0.30×10^{-6}	yellow
2	Ti = 48	,,	TiO_2: ,,	0.0195	,, $\times 0.22$	0.7×10^{-7}	orange
3	Mo = 96	,,	MoO_3: ,,	0.1080	,, $\times 0.22 \times 10^{-3}$	no reducing action	yellow
4	V = 51	,,	V_2O_5: ,,	0.3107	,, $\times 0.3 \times 10^{-10}$	do.	reddish browh
5	Cr = 52	,,	CrO_3: ,,	0.4802	—	—	blue

The above table shows that the concentrations of hydrogen peroxide in the "Per-acids" are gradually decreased in the order of U, Ti, Mo, V and Cr; the decreases of partial vapor pressure of the peroxide in these cases being also parallel to the quantity above mentioned. Considering from these points, it is clear that the degree of freedom of hydrogen peroxide in the "Per-acids" are restricted in the order above mentioned. In other words, the combinations of hydrogen peroxide with the "Acid nucleus" in the unstable "Per-acids" are firmer and stronger than those in the stable ones. And here exists, indeed, the key to the problem of clearing up the true nature of "Per-acids." The reason is that, from the above conjecture we know that the combining forces exerted between hydrogen peroxide and "Acid nucleus" are related very closely with the stability and colour of the "Per-acids."

G. N. Lewis[1] once published an opinion on the colour of the chemical substances that the compounds in which electrons are most firmly constrained have no colour; but when the constraints become gradually weaker, they begin to absorb the visible part of the spectrum, from longer wavelength to shorter and they show from yellow to orange or red; and finally, when the constrains reach its loosest condition, they absorb the red or ultra red part in the spectrum, and the colour of the compounds become blue. This theory also throws a light upon the true nature of "Per-acids."

As is clearly know from Postulate II, any arbitrary inductor is not capable of inducing any arbitrary acceptor. This is the reason why those elements situated in the early period of the periodic table show a more pronounced property as "Oxy-acids" than as "Per-acids." The "Acid nuclei" of C, N and S are readily induced by water as an inductor but not by hydrogen peroxide except under special conditions.

Next considerations will be given upon the case of Ti, V and Cr, whose atomic weights are larger than the preceding case. The "Acid nuclei" of these elements are as shown below:

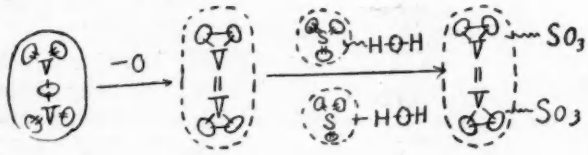


"Titanic acid nucleus" "Vanadic acid nucleus" "Chromic acid nucleus"

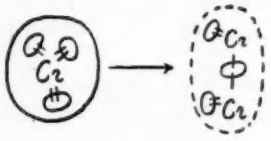
Glancing at the configurations of the "Nuclei" of the acids, one will perceive that they well explain the gradual alterations manifested in the properties of these acids. The "Nuclei" which possess as much mass as in these elements are induced both by hydrogen peroxide and water as inductors. Among them (2) and (3) are coloured; the fact means that some electrons whose constraints are loose in some parts, and the "Nuclei" are readily inducable by inductors. This is the reason why V and Cr have a marked tendency to form "Per-acids." In the case of Ti, the loose combining force of hydrogen peroxide with the "Acid nucleus" is due to its comparatively stable configuration. Next in acid solutions, "Per-vanadic" and "Per-chromic"-acids decompose very rapidly and evolve oxygen, the blue and greenish blue colourations of vanadyl ion and trivalent chromium

(1) Loc. cit.

respectively being finally produced. In these cases, the electrical displacement produced on the formation of "Per-acids" is so remarkable that the constraints upon some of the electrons are loosened over a definite range and the "Nuclei" suffer such fundamental alterations as mentioned above. The phenomena will most conveniently be represented by the following scheme.

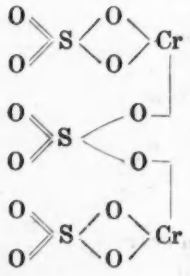


"Vanadic acid nucleus" "Hypovanadic acid nucleus" Two molecules of sulphuric acid Vanadyl sulphate Water



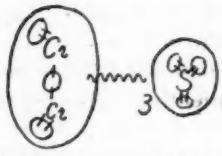
"Chromic acid nucleus" "Chrome amphoteric nucleus"

Such group as is shown in the right hand side of (4) is called "Amphoteric Nucleus." Reviewing from the standpoint of "Induction valence," such a salt as chromic sulphate which is readily hydrolized must be considered from a different point of view. The constitutional formula commonly given to chromic sulphate is represented as follows.



..... (5)

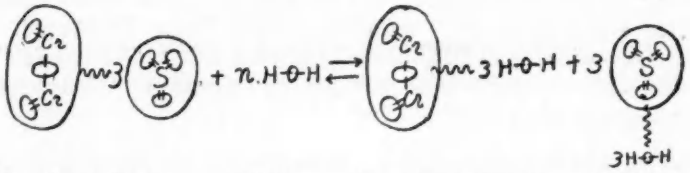
But by (5), the readiness with which this salt is hydrolized can hardly be explained. The "Induction valence theory," therefore, substitutes (6) for (5)



(6)

"Chrome amphoteric nucleus" "Sulphuric acid nucleus"

Then the phenomenon of hydrolysis will be represented by the following.



(7)

Chromium sulphate Water Chromium hydroxide Sulphuric acid

It is clear that (7) explains the phenomenon very easily. The fact that Al and Cr are not readily deposited from its salt solution by electrolysis will also be conveniently explained by considering the presence of such a "Nucleus."

Now, a consideration will be given upon the case of Mo whose atomic weight is larger than the preceding case. In this case, the constraints upon the electrons is firm and strong as is known from the fact that MoO_3 is colourless. The electrical displacement due to "Induction" is accordingly small and the resulting "Per-acid" is yellow in colour and more stable than those of V and Cr.

The case of U will next be considered. As the mass of the "Uranic acid nucleus" is large, it is easily understood that the "Nucleus" will not be readily induced by the inductor as has been already explained in Postulate II. This is the reason why the freedom of hydrogen peroxide is largest in the case of "Per-uranic acid." The inertia to "Electrical induction" in this case, however, must be considered large, and the resulted "Per-acid" stable.

Finally, an explanation will be given upon the diversity of the compositions of "Per-acids" isolated. As has been mentioned already, the combination of "Acid nucleus" with hydrogen peroxide is accomplished by "Induction valence." It is, therefore, partly dependent on the dielectric constant of the medium, and a different medium will give a different dielectric constant. The diversity of the compositions is, therefore, nothing

but a natural consequence of the above reason. This is also the case that there exist various kinds of phosphoric acid.

By the descriptions given above the present author believes that the true aspects of his "Acid nucleus theory" which explains the true natures of "Oxy-acids" or "Per-acids" have been rendered clear. He is also eager to extend his theory to the other problems in chemistry in the near future.

Summary.

1. Starting from three postulates, the presence of "Acid nuleus" has been considered and a new idea "Induction valence" also introduced.

2. That "Oxy-acids" and "Per-acids" are nothing but "Acid nuclei" combined with water or hydrogen peroxide by means of "Induction valence" has been rendered clear.

In conclusion, the author wishes to acknowledge his obligations to Profs. M. Kobayashi, F. Ishikawa and S. Mitsukuri in the Institute of Chemistry, Faculty of Science for their useful suggestions and Prof. T. Murakami, in the Institute of Metallurgy, Faculty of Engineering for the encouragement given to him.

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